Technical Paper 5

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
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THE CONSTITUENTS OF COAL SOLUBLE IN PHENOL

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WASHINGTON
GOVERNMENT PRINTING OFFICE
1912

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THE CONSTITUENTS OF COAL SOLUBLE IN PHENOL.

By J. C. W. Frazer and E. J. Hoffman.

INTRODUCTION.

This paper presents some results of an investigation of the nature of the chemical compounds that go to make up the complex material known as coal. The investigation was begun by the technologic branch of the United States Geological Survey and is being continued by the Bureau of Mines as one of several inquiries conducted in connection with the analyzing and testing of mineral fuels. The aim of these inquiries is to obtain definite information regarding the composition of coal and the nature of its constituents. In spite of all the advances in the study of the products of the destructive distillation of coal, and in spite of the great chemical industries that have resulted from the knowledge gained by that study, little is definitely known regarding the chemical nature of coal itself. The need of such information is deemed sufficient reason for the inception and continuance of these inquiries.

The problem of the chemical constitution of coal is not only of scientific interest, but is also of much importance from the standpoint of the commercial world, because solution of the great problems involved in the technical treatment of coal can scarcely be expected without further knowledge regarding the chemical nature of the substances in coal.

Manifestly, if so little progress has been made in so important a field of research, there must be some special reason for the fact. An explanation more than adequate is to be found in the extreme difficulty of finding a satisfactory point of attack, owing to the great resistance of the coal substance to the action of the ordinary solvents and reagents.

In attempting to solve the problem the chemist has at hand no well formulated methods, and finds available only scattered and fragmentary data. Up to the present time the destructive distillation of coal has given little information that may serve as a guide. There are, however, two other distinct methods of procedure, one or both of which may be followed to advantage. One of these calls for the conversion of the coal substance into recognizable derivatives; the other involves extraction by means of solvents and the identification of the constituents thus separated.

A number of investigators have followed these methods with more or less promise of success. The scope of this paper, however, does not permit a discussion of their investigations nor the consideration of any contributions that they have made to the knowledge of the subject.

METHOD OF EXTRACTING COAL WITH PHENOL.

In addition to the study reported in this paper, the authors have made a number of preliminary investigations of the action on coal of several different chemical reagents and of practically all the ordinary organic solvents. In the main, however, the experiments have been confined to the extraction of coal with solvents. Of all the solvents used, phenol, pyridin, and anilin removed from the several coals examined the largest quantities of soluble material. It was decided to study in some detail the phenol-soluble constituents of one coal. A noncoking bituminous coal from Zeigler, Franklin County, Ill., was selected; it had the following composition:

Analysis of coal from Zeigler, Ill.

Proximate analysis.			Ultimate analysis.		
Determination.	As received.	Moisture and ash free.	Determination.	As received.	Moisture and ash free.
Moisture	11.82		Hydrogen	5.44	4.99
Volatile matter	27.66	33.43	Carbon	67.87	82.01
Fixed carbon	55.10	66.57	Oxygen	19.47	10.83
Ash	5.42		Sulphur	.46	.55
			Nitrogen	1.34	1.62
			Ash	5.42	
	100	100		100	100

The vessel in which the coal was extracted with phenol was simply a double-walled cylinder of tinned copper, its inner compartment being 60 cm. in height and 10.5 cm. in diameter. In the bottom of this compartment were a number of small perforations; below the perforated bottom the sides formed a funnel, through which the phenol solution could be drawn off by suction. The outer compartment contained water or phenol, which was heated during the extraction by means of a ring burner placed beneath the vessel.

Upon the perforated bottom of the inner compartment a filter was carefully prepared. This filter was made of macerated filter paper, or a mixture of the latter with sand. The finely ground coal, intimately mixed with molten phenol, was poured into the extraction vessel and heated by means of the hot liquid in the outer compartment. After being heated for about 10 hours, the liquid was drawn off through the filter and refiltered, while hot, on a Büchner funnel. Although no attempt was made to effect a quantitative extraction, the coal residue was extracted with fresh phenol until practically all the soluble material had been removed. Usually three or four extractions were sufficient for 1,000 grams of coal.

The temperature of extraction varied considerably; ordinarily this temperature was 140° C. when phenol instead of water was used in the outer compartment. The authors consider such heating undesirable and in future will perform all extractions at ordinary temperatures.

The filtered solution, which was dark red in color, was concentrated under diminished pressure on an oil bath, at a temperature of 105 to 115° C., to a thick tarlike mass. This mass hardened on cooling, but could be removed from the distilling flask by treatment with enough sodium hydroxide solution to take up all the phenol present. After the mixture had been removed from the flask and triturated, the liquid and the suspended matter were acidified with hydrochloric acid and filtered by suction. The mass on the filter was washed with water until a washing showed only a trace of chlorine. It was practically impossible to wash out the last traces of phenol from the material. The extract was freed from water as much as possible with the aid of the filter pump and was then allowed to dry in the air for a short time. The nature of the subsequent treatment of the extract made further drying of the material unnecessary.

The filtrate and washings were slightly red in color and contained a small part of the extracted material, but the quantities were so slight that their recovery was considered impracticable.

The coal at the time of treatment contained 9 per cent of moisture; had it been dry, the solvent action of the phenol no doubt would have been more effective. From 4,230 grams of the coal there were obtained 489 grams of partly dried extract containing 17.21 per cent of moisture and 2.48 per cent of ash; or, on a moisture and ash free basis, from 3,613 grams of pure coal substance the phenol removed 393 grams, or 10.87 per cent.

THE PHENOL EXTRACT.

The crude extract P[a] was a dark-brown mass very similar in appearance to the original coal; when finely powdered it was brown and sticky. A sample of the material was washed with water, dried in a desiccator containing phosphorus pentoxide, and analyzed. The ultimate analysis showed the following composition.

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[a] The letters and figures used to designate the various fractions of the coal extract refer to Plate I, which presents an outline of the procedure followed and the ultimate analysis and molecular weights of the substances.

Analysis of extract P.

Determination.	Found.	Calculated to ash-free basis.
C	79.88	81.64
H	5.70	5.83
O	10.62	10.85
S	.37	.38
N	1.27	1.30
Ash	2.16	....
	100	100

The greater part (424 grams) of the phenol extract was treated with a 10 per cent solution of sodium hydroxide to effect further separation. The operation consisted in repeatedly shaking 60 to 80 gram portions of the powdered material with alkali solution in a flask, filtering after each treatment, returning the undissolved residue to the flask, and repeating the treatment with fresh solution until the filtrate from the material was only faintly colored. The residue was washed well with water, but no attempt was made to remove the last traces of sodium hydroxide.

Extraction and filtration were extremely slow and tedious operations. The first filtration was effected on a Büchner funnel, the filter being a closely woven cloth that had been boiled in alkali solution and washed with water. But this filtration was by no means perfect, and the solution had to be refiltered through "hardened" filter paper previously washed with alkali.

Before the material in solution was precipitated, sulphur dioxide was passed through the solution for several hours in order to reduce any oxidation products that, it was feared, might have formed during the long process of filtration. Hydrochloric acid was then added a little at a time, and the mixture was kept cool until precipitation was complete. The bulky, flocculent, dark-brown precipitate was brought upon the filter of hardened paper and washed several times with dilute hydrochloric acid. It was then returned to the flask, shaken with water, and again brought upon the filter. The shaking with water was repeated several times, as the mass was so slimy that washing on the filter alone was not effective. Washing with water on the filter was continued until only a trace of chlorine could be detected in the washings. The bulky mass in drying contracted to about one-tenth the volume it had when wet. The drying was completed over calcium chloride in a vacuum desiccator.

THE SODIUM HYDROXIDE EXTRACT OF FRACTION *P*.

The sodium hydroxide extract, *A*, of the crude extract, *P*, when dry and finely powdered was similar in appearance to the phenol extract, but was slightly browner, and more sticky. The sodium

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hydroxide dissolved 58 grams, nearly 17 per cent, of the phenol extract, and 1.84 per cent of the original coal. The extract contained 0.54 per cent of ash.

By extraction of this material in a Soxhlet apparatus with anhydrous ether distilled over sodium, an ether extract weighing 16 grams, equal to 0.51 per cent of the coal, was obtained.

The residue *D*, insoluble in ether, was digested with hydrochloric acid, filtered, washed with water, dried over phosphorous pentoxide, and analyzed. Its composition was:

Analysis of extract A.

Determination.	Found.	Calculated to ash-free basis.
C	73.13	75.76
H	4.85	4.89
O	17.17	17.32
S	.79	.80
N	1.22	1.23
Ash	.84	....
	100	100

THE ETHER EXTRACT OF *A*.

The ether extract of *A* was a dark-red, viscous, sticky mass, *C*, somewhat resembling molten pitch; it had a pleasing odor. It was readily soluble in ether, the color of the solution varying from yellow to deep red as the concentration increased.

After the removal of the ether by distillation on the water bath, the substance was distilled under diminished pressure. It was distilled on an oil bath up to a temperature of 230° C., and on a graphite bath above that temperature. The receiver for each fraction, a small flask, was cooled by a mixture of salt and ice.

At a temperature of 40° C., under an absolute pressure of 15 to 30 mm. of mercury, a colorless distillate came over; the quantity was too small for examination. The distillate, I, probably consisted largely of ether, for it had the odor of ether.

At 130 to 150° C. and 6 to 10 mm., the distillate was a greenish yellow liquid, II, having a very agreeable aromatic odor; the quantity was too small to examine. The third fraction, which came over at 200 to 230° C. and 1 to 3 mm., was a reddish yellow substance, III, which solidified in the stem of the distilling flask. This substance was redistilled. At 90 to 100° C., 1 mm. pressure, a liquid resembling phenol came over; at 100 to 200° C., 2 to 4 mm., the distillate was a yellow oil of pleasing aromatic odor, accompanied by a very few white crystals that came over at a temperature of 110 to 145° C. The quantity of neither of these distillates was large enough for examination.

The residue of III remaining in the distilling flask was treated with hot methyl alcohol. The insoluble portion melted under the alcohol and on cooling formed flat white crystals. These crystals were dissolved in ether and recrystallized. Their melting point was 59 to 60° C.

The distillation of *C* was continued under a pressure of 1 mm. and yielded two fractions; one, IV, at 230 to 255° C., the other, V, at 260 to 300° C. During the distillation small white crystals were deposited in the neck of the distilling flask and on the under part of the stopper. These crystals had a melting point of 154 to 171° C. The two fractions were combined and redistilled at a pressure of 1 to 2 mm. Three fractions were obtained: A, at 60 to 125° C., a yellow liquid in which white crystals formed; B, at 125 to 160° C., a similar distillate; and C, at 160 to 213° C., a yellow paraffin-like solid.

From fraction B massive blocks of crystals of a greenish yellow color separated. These crystals were dried on a porous plate and redissolved in ether, from which solution slender feather-like crystals were obtained that at 137 to 168° C. melted with decomposition. They were probably identical with the crystals that were deposited during the previous distillation of *C* at a temperature of 230 to 300° C. Their percentage composition was: C, 60.00; H, 7.06; O, 32.94.

The yellow solid substance, C, melted at 48 to 50° C. It had the following composition: C, 78.38; H, 7.14; O, 14.48 per cent. This composition corresponds closely to the empirical formula, $C_{65}H_{71}O_9$.

From the residue of the distillation of IV and V, after removal of the portion soluble in methyl alcohol, there were obtained a very few white crystals that had a melting point of 50 to 60° C. These appeared to be identical with those obtained from the residue of III.

Of the 16 grams of *C* a residue of 9 grams remained undistilled. This was a mixture of black and yellow substances; the yellow substances were soluble in chloroform.

THE PORTION OF THE PHENOL EXTRACT, *P*, INSOLUBLE IN SODIUM HYDROXIDE.

The portion (fraction *B*) of the phenol extract insoluble in sodium hydroxide was dried over calcium chloride and extracted with anhydrous ether in a Soxhlet apparatus. At the beginning of the extraction, the solution in ether was greenish yellow and exhibited a beautiful green fluorescence; as the extraction progressed, the soluble matter colored the ether intensely red. In the last stages of the extraction the solution obtained was light yellow in color, and this color was imparted to fresh ether even after extraction had been in progress for more than a week. This coloration and the fact that a small quantity of a dark-brown solid substance was deposited in the extraction flask, indicated that a part of the material was only slightly soluble in ether. The combined ether solutions were filtered, the ether was distilled off, and the extract was dried on the water bath and weighed. From 264 grams of *B* the ether removed 55 grams of extract, equal to 1.75 per cent of the weight of the coal.

THE ETHER EXTRACT OF *B*.

The ether extract of *B* was a sticky, viscous, red mass, *E*, that had a pleasant aromatic odor, and closely resembled in appearance and odor the corresponding ether extract obtained from the portion of the phenol extract soluble in alkali. By treatment with pure petroleum ether, boiling point 40 to 70° C., a deep-red solution, not unlike the solution in ethyl ether, was obtained; this, on removal of the solvent, yielded about 20 grams of a sticky dark-red liquid, *F*, having the same odor as the ether extract. This dark-red liquid was separated by means of pure methyl alcohol into a soluble fraction, *K*, and an insoluble fraction, *L*. The portion of the ether extract, *E*, insoluble in petroleum ether, *G*, was a sticky brownish yellow powder. Absolute ethyl alcohol extracted from this powder a stiff, red, pitchlike mass, *H*, and left an insoluble dark-red solid, *I*.

The four fractions, *H*, *I*, *K*, *L*, obtained from the ether-soluble substance were at this stage tested for nitrogen and sulphur. In none of them was either nitrogen or sulphur found.

In the further examination of these fractions molecular weight determinations of the substances obtained by subsequent fractionation were made when the quantity of material available permitted. These determinations were made in many instances solely for the purpose of comparison, and the values obtained are given herein as molecular weights; but it is not to be inferred that in these instances the authors consider that the substances are probably pure or individual compounds. The determinations were made by the freezing-point method, pure benzene being used as the solvent in all determinations, unless another solvent is mentioned.

Owing to the small proportion of oxygen in the several fractions obtained from *K* and *L* and the large error consequently possible in determining oxygen by difference, empirical formulas based on the oxygen content could not be derived with certainty from the analyses. For this reason the formulas given for these substances were derived from the percentage composition and the molecular weight of the substances. The procedure was followed also in deriving the empirical formulas for the substances obtained from the fractions *H* and *I*.

Before a substance was analyzed or its molecular weight was determined, it was warmed at a temperature of 50 to 80° C. and a pressure of about 1 mm. for several hours, to remove the last traces of the solvent.

THE METHYL ALCOHOL EXTRACT OF *F*.

The total weight of the methyl alcohol extract of *F* was 8 grams, or 0.26 per cent of the weight of the coal. This substance, *K*, was a sticky, viscous, dark-red liquid, possessing an extremely agreeable aromatic odor.

Four samples were analyzed with the following results:

Analyses of K.

(1) 0.2588 gram substance gave 0.8281 gram CO_2 and 0.1908 gram H_2O.
Percentage composition: C, 87.27; H, 8.19; O, 4.54.
(2) 0.1149 gram substance gave 0.3681 gram CO_2 and 0.0825 gram H_2O.
Percentage composition: C, 87.37; H, 7.98; O, 4.65.
(3) 0.1246 gram substance gave 0.3989 gram CO_2 and 0.0930 gram H_2O.
Percentage composition: C, 87.31; H, 8.29; O, 4.40.
(4) 0.1858 gram substance gave 0.5934 gram CO_2 and 0.1381 gram H_2O.
Percentage composition: C, 87.10; H, 8.26; O, 4.64.

The molecular weight determination gave the value 285. The formula $C_{21}H_{23}O$ (molecular weight, 291), derived from the mean of the four analyses and the molecular weight value 285, requires: C, 86.60; H, 7.90; O, 5.50 per cent.

The greater part (5.5 grams) of the substance *K* was next subjected to distillation in a vacuum. By vacuum is meant the lowest pressure attainable with the latest modification of the Geissler mercury air pump. At a temperature of 133 to 160° C. there distilled over a light yellow oil, *1*, in which, on cooling, white crystals were observed. The distillate that came over at 160 to 201° C. was a mixture, *2*, of yellow and red liquids, the red portion distilling at 190 to 201° C. By redistillation there were obtained from *1* two fractions, *1a*, at 85 to 107° C., and *1b*, at 107 to 165° C. In like manner there were obtained from *2* three fractions: *2a*, at 130 to 153° C.; *2b*, at 153 to 163° C., and *2c*, at 163 to 201° C. The total weight of these five fractions was very little more than 1 gram and was less than 0.1 per cent of the weight of the coal.

The fraction *1a* was a light yellow oil that had an aromatic odor. An analysis resulted as follows:

0.1188 gram substance gave 0.3862 gram CO_2 and 0.0977 gram H_2O.
Percentage composition: C, 88.66; H, 9.14; O, 2.20.

Fraction *1b*, a yellow oil containing greenish white crystals and having an odor slightly different from that of *1a*, was treated with methyl alcohol. The soluble part was a mixture of a yellow oil and greenish white crystals. The impure crystals melted at 162 to 169° C. On analysis—

0.1566 gram crystals gave 0.4999 gram CO_2 and 0.1118 gram H_2O.
Percentage composition: C, 87.06; H, 7.93; O, 5.01.

The insoluble part of *1b* was a mixture of a reddish yellow oil and a very few crystals that had a melting point of 160 to 165° C. On analysis—

0.2399 gram substance gave 0.7811 gram CO_2 and 0.1864 gram H_2O.
Percentage composition: C, 88.80; H, 8.63; O, 2.57.

Fraction *2a* was a deep-yellow oil, of aromatic odor, in which white feather-like crystals were suspended. The melting point of the impure crystals was 175 to 193° C.

Fraction *2b* was a red viscous oil, and fraction *2c* was a red oil similar to *2b*, but thicker.

Analyses of these fractions gave the following results:

Analyses of fractions 2a, 2b, and 2c.

Fraction *2a*.

0.1650 gram substance gave 0.5282 gram CO_2 and 0.1204 gram H_2O.
Percentage composition: C, 87.31; H, 8.11; O, 4.58.
The molecular weight was 241.
Calculated for $C_{18}H_{20}O$ (molecular weight, 252): C, 85.71; H, 7.93; O, 6.35.

Fraction *2b*.

0.1527 gram substance gave—
0.4867 gram CO_2 and 0.1091 gram H_2O.
Percentage composition: C, 86.92; H, 7.94; O, 5.14.
The molecular weight was 267.
Calculated for $C_{19}H_{21}O$ (molecular weight, 265): C, 86.04; H, 7.93; O, 6.03.

Fraction *2c*.

0.1073 gram substance gave 0.3429 gram CO_2 and 0.0768 gram H_2O.
Percentage composition: C, 87.15; H, 7.95; O, 4.90.
The molecular weight was 279.
Calculated for $C_{20}H_{22}O$ (molecular weight, 278): C, 86.33; H, 7.91; O, 5.76.

The residue left in the above distillation of *K* was very much like the original mass, but more viscous. On analysis—

0.1934 gram substance gave 0.6164 gram CO_2 and 0.1347 gram H_2O.
Percentage composition: C, 86.92; H, 7.74; O, 5.34.
The molecular weight was 401.
Calculated for $C_{29}H_{31}O$ (molecular weight, 395): C, 88.10; H, 7.85; O, 4.05.

THE PORTION OF THE PETROLEUM-ETHER EXTRACT, *F*, INSOLUBLE IN METHYL ALCOHOL.

The portion of the petroleum-ether extract, *F*, insoluble in methyl alcohol and designated as *L* in figure 1, was about 60 per cent of the total material soluble in petroleum ether. In appearance and odor it resembled closely the portion of the petroleum-ether extract that was soluble in the alcohol, but it was more viscous. On analysis:

0.2240 gram substance gave 0.7184 gram CO_2 and 0.2024 gram H_2O.
Percentage composition: C, 87.47; H, 10.04; O, 2.49.
The molecular weight was 404.
Calculated for $C_{29}H_{41}O$ (molecular weight, 405): C, 85.92; H, 10.12; O, 3.96.

On vacuum distillation, at a temperature of 133 to 201° C., 5 grams of the substance yielded about 1 gram of distillate, or less than 0.1 per cent of the coal. This distillate, a mixture of a yellow and a reddish yellow oil with a waxy solid, was redistilled.

At 100 to 166° C., a lemon-yellow oil, *a*, possessing the odor of rancid butter combined with a peculiar and pleasant odor, was obtained.

At 173 to 177° C., the distillate was a thick pink oil, *b*, that showed traces of white crystals and had an odor like the agreeable part of the odor of *a*.

The third fraction, *c*, distilled at a temperature of 190 to 201° C., was a lemon-yellow solid substance of greasy appearance and having an odor like that of the original, *L*.

Analyses of these fractions gave the following results:

Analyses of fractions a, b, and c.

Fraction *a*.

0.1696 gram substance gave 0.5429 gram CO_2 and 0 1597 gram H_2O.
Percentage composition: C, 87.31; H, 10.40; O, 2.29.
The molecular weight was 255.
Calculated for $C_{19}H_{27}O$ (molecular weight, 271): C, 84.13; H. 9.96; O, 5.91.

Fraction *b*.

0.0850 grams substance gave 0.2753 gram CO_2 and 0.0793 gram H_2O.
Percentage composition: C, 88.33; H, 10.37; O, 1.30.

Fraction *c*.

0.1474 gram substance gave 0.4764 gram CO_2 and 0.1394 gram H_2O.
Percentage composition: C, 88.15; H, 10.51; O, 1.34.
The molecular weight was 337.
Calculated for $C_{25}H_{35}O$ (molecular weight, 351): C, 85.47; H, 9.97; O, 4.56.

The residue of *L*, a hard, pitch-like, red mass, was analyzed. The analysis resulted as follows:

0.1915 gram substance gave 0.6154 gram CO_2 and 0.1675 gram H_2O.
Percentage composition: C, 87.64; H, 9.72; O, 2.64.
The molecular weight was 460.
Calculated for $C_{34}H_{45}O$ (molecular weight, 469): C, 87.00; H, 9.59; O, 3.41.

THE ABSOLUTE ALCOHOL EXTRACT OF *G*.

About 80 per cent of *G*, less than 1 per cent of the coal, was soluble in absolute ethyl alcohol. The solution was deep red. On evaporation of the alcohol a hard red cake of material was obtained, which, when powdered, gave a sticky, reddish yellow substance. This substance, *H*, was further separated by means of cold methyl alcohol into a soluble and an insoluble fraction. The soluble substance, *M*, was a sticky, reddish yellow powder; the insoluble substance, *N*, was very similar in appearance to *M*, but was more nearly yellow, having only a faint tinge of red.

To remove any material that had possibly escaped previous solution in petroleum ether, *M* was triturated several times with fresh portions of that solvent and filtered. The residue was then dissolved in a very little ethyl ether; when much ethyl ether was used a brown gummy substance was formed. By evaporating off the greater part of the ether, most of the gummy substance was redissolved, leaving a small residue, *MR1*. The ether solution was poured slowly into four or five times its volume of petroleum ether while the petroleum ether was constantly stirred. A brownish yellow powder, *Ma,* was precipitated, together with a red gummy substance, *MR2*. The yellow precipitate, *Ma,* was poured off upon a filter and the gummy substance, *MR2,* retained in the beaker. Upon concentrating the filtrate and repeating the precipitation, two additional substances, *Mb* and *Mc,* of deep red color were obtained. After drying, the brownish yellow powder, *Ma,* was no longer entirely soluble in ether. The insoluble portion, *MaR,* was similar to *MR2*. The soluble portion was reprecipitated with petroleum ether and yielded a canary-yellow powder *M1*. The second and third precipitates, *Mb* and *Mc,* were combined and likewise precipitated, as indicated by *M2* in Plate I. The total weight of *M1* obtained in the above way was less than 1 gram, or 0.03 per cent of the coal; the other substances were in smaller quantities.

The melting point of none of the fractions of *M* could be determined on account of decomposition. Analyses of these fractions resulted as follows:

Analyses of fractions of M.

Fraction *MR1.*

0.1523 gram substance gave 0.4533 gram CO_2 and 0.0848 gram H_2O.

Percentage composition: C, 81.60; H, 6.22; O, 11.68; ash, 0.50. Calculated to an ash-free basis: C, 82.01; H, 6.25; O, 11.74.

The molecular weight (in nitrobenzene) was 450.

Fraction *MR2*

0.1814 gram substance gave 0.5631 gram CO_2 and 0.1205 gram H_2O.

Percentage composition: C, 84.66; H, 7.38; O, 7.96.

The molecular weight was 399.

Calculated for $C_{28}H_{29}O_2$ (molecular weight, 397): C, 84.64; H, 7.30; O, 8.06.

Fraction *MaR.*

0.0660 gram substance gave 0.2107 gram CO_2 and 0.0324 gram H_2O.

Percentage composition: C, 87.07; H, 5.45; O, 7.48.

Fraction *M1.*

0.0895 gram substance gave 0.2720 gram CO_2 and 0.0522 gram H_2O.

Percentage composition: C, 82.88; H, 6.48; O, 10.64.

The molecular weight (in nitrobenzene) was 393.

Calculated for $C_{27}H_{25}O_3$ (molecular weight, 397): C, 81.61; H, 6.29; O, 12.09.

Fraction *M2.*

0.0756 gram substance gave 0.2291 gram CO_2 and 0.0448 gram H_2O.

Percentage composition: C, 82.65; H, 6.58; O, 10.77.

The determination of the molecular weight of this substance, *M2*, was of doubtful accuracy because of the small quantity of the substance available for the determination. The value found was 338, but the value probably should have been more nearly that of *M1*, as in composition and appearance *M1* and *M2* were practically identical.

The yellow powder *N* was treated in the same way as was *M*. After removal of anything soluble in petroleum ether, the substance all dissolved in ether except a small dirty-black residue, *NR1*. With petroleum ether, two precipitates, *Na* and *Nb*, were obtained. After *Na* was dried it could not be entirely redissolved in ether, but left a dark-red residue, *NaR*. Two successive precipitations of the soluble part gave *N1* and *N2* light-yellow powders. In the same way, from *Nb* were obtained *N3* and *N4*, which were similar to *N1* and *N2*, but had a decided red tinge. The fractions of *N* thus obtained were about the same in quantity as those of *M*. Analyses gave the following results:

Analyses of fractions of N.

Fraction *N1*.

0.0967 gram substance gave 0.2935 gram CO_2 and 0.0548 gram H_2O.
Percentage composition: C, 82.78; H, 6.29; O, 10.93.
The molecular weight (in nitrobenzene) was 514.
Calculated for $C_{35}H_{32}O_3$ (molecular weight, 500): C, 84,00; H, 6.40; O, 9.60.

Fraction *N2*.

0.0905 gram substance gave 0.2829 gram CO_2 and 0.0561 gram H_2O.
Percentage composition: C, 85.25; H, 6.89; O, 7.86.
The molecular weight was 600.
Calculated for $C_{43}H_{41}O_3$ (molecular weight, 605): C, 85.29; H, 6.78; O, 7.93.

Fraction *NR1*.

0.1000 gram substance gave 0.3023 gram CO_2 and 0.0554 gram H_2O.
Percentage composition: C, 82.45; H, 6.18; O, 10.37; ash, 1.00.
Calculated to an ash-free basis: C, 83.28; H, 6.24; O, 10.48.

Fraction *NR2* (two samples).

I. 0.1418 gram substance gave 0.4443 gram CO_2 and 0.1005 gram H_2O.
Percentage composition: C, 85.45; H, 7.87; O, 6.68.
II. 0.1364 gram substance gave 0.4289 gram CO_2 and 0.0956 gram H_2O.
Percentage composition: C, 85.76; H, 7.79; O, 6.45.
The molecular weight was 450.
Calculated for $C_{32}H_{35}O_2$ (molecular weight, 451): C, 85.14; H, 7.76; O, 7.10.

Fraction *NaR* (two samples).

I. 0.1049 gram substance gave 0.3215 gram CO_2 and 0.0606 gram H_2O.
Percentage composition: C, 83.58; H, 6.42; O, 10.00.
II. 0.1030 gram substance gave 0.3168 gram CO_2 and 0.0576 gram H_2O.
Percentage composition: C, 83.88; H, 6.21; O, 9.91.
The molecular weight (in nitrobenzene) was 488.
Calculated for $C_{34}H_{31}O_3$ (molecular weight, 487): C, 83.78; H, 6.37; O, 9.85.

THE PORTION OF *G* INSOLUBLE IN ABSOLUTE ALCOHOL.

The portion of *G* insoluble in absolute alcohol (*I*, Plate I) was about 20 per cent of *G*. It was a red-brown powder almost entirely soluble in benzene. Its behavior during the attempt to determine its melting point was noted. At 140° C. it began to shrink and darken; at 160° C. it began to melt; at 170° C. it had melted entirely. The insoluble portion, *Ib*, was darker than the soluble portion, and had a very dirty appearance. The portion of *I* soluble in benzene, *Ia*, and the portion insoluble in benzene, *Ib*, were analyzed with the following results:

Analyses of the portions of I.

Portion *Ia.*

0.2258 gram substance gave 0.7094 gram CO_2 and 0.1386 gram H_2O.
Percentage composition: C, 85.64; H, 6.82; O, 7.54.
The molecular weight was 631.
Calculated for $C_{45}H_{43}O_3$ (molecular weight, 631): C, 85.58; H, 6.81; O, 7.61.

Portion *Ib.*

0.1416 gram substance gave 0.4304 gram CO_2 and 0.0746 gram H_2O.
Percentage composition: C, 82.90; H, 5.85; O, 10.25; ash, 1.00.
Calculated to an ash-free basis: C, 83.74; H, 5.91; O, 10.35.

THE PORTION OF *B* INSOLUBLE IN ETHER.

The residue, *R*, of the phenol extract that remained after the successive treatments with sodium hydroxide and ether was about 60 per cent of the whole. Of this residue, 18 per cent was soluble in hot glacial acetic acid, forming a dark-red solution. When this solution cooled a brown substance, *R1*, was deposited from it. This substance was washed with ammonia, then with water, dried over phosphorus pentoxide, and analyzed. Analysis showed the following composition:

C, 80.48; H, 6.14; O, 10.22; N, 1.62; S, 0.38; ash, 1.16 per cent. Calculated to an ash-free basis: C, 81.42; H, 6.21; O, 10.34; N. 1.64; S, 0.39.

The filtrate of *R1*, when evaporated to dryness on the water bath, left a sticky dark-red mass; this, when powdered, was similar in appearance to red phosphorus. Extraction of the mass with ether removed a brown-red substance, which on precipitation in petroleum ether, became a reddish-yellow powder, *R2a*. This powder was washed, dried, and analyzed. Analysis showed the following composition:

C, 80.82; H, 6.56; O, 7.10; N, 4.29; S, 0.40; ash, 0.83. Calculated to an ash-free basis: C, 81.50; H, 6.61; O, 7.16; N, 4.33; S, 0.40.

The residue, *R2b*, insoluble in ether, was a brown powder that had the following composition:

C, 77.55; H, 5.90; O, 12.58; N, 2.05; S, 0.35; ash, 1.57. Calculated to an ash-free basis: C, 78.79; H, 6.00; O, 12.78; N, 2.08; S, 0.35.

The residue of *R* insoluble in hot acetic acid, washed with ammonia and water and then dried, had the following composition:

C, 79.29; H, 5.19; O, 12.55; N, 1.83; S, 0.40; ash, 0.74. Calculated to an ash-free basis: C, 79.88; H, 5.23; O, 12.65; N, 1.84; S, 0.40.

CONCLUSIONS.

Plate 1 presents an outline of the method of separation described in the preceding pages. The analyses recorded in this figure are the mean of all determinations for a given substance on a moisture and ash-free basis.

In the lack of evidence to the contrary, it is assumed that the coal substance soluble in phenol is present as such in the coal itself.

The authors believe, as a result of the investigation described in this paper, that some of the substances isolated very closely approach pure compounds. That any of them are such compounds could not be established, from lack of a sufficient quantity of substance for study. Some of the substances appear to be almost pure hydrocarbons, containing small quantities of oxygenated compounds, but any conclusion as to their real nature is evidently premature.

However, the investigation demonstrated that success may be expected from this method of attempting to determine the constituents of coal, provided larger quantities of the substances isolated can be obtained for examination. For that reason a second investigation is in progress. In this investigation large quantities of coal are being extracted with pyridin; when a large quantity of the pyridin-soluble substance of coal has been accumulated it will be studied in a similar way.

PUBLICATIONS ON FUEL TESTING.

PUBLICATIONS OF THE BUREAU OF MINES.

The following publications may be obtained without cost by applying to the Director, Bureau of Mines, Washington, D. C.

Bulletin 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl.

Bulletin 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

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Bulletin 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp.

Bulletin 13. Résumé of producer-gas investigations, October 1, 1904–June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls.

Bulletin 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908–9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls.

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Bulletin 21. The significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 64 pp. Reprint of United States Geological Survey Bulletin 367.

Bulletin 24. Binders for coal briquets, by J. E. Mills. 56 pp. Reprint of United States Geological Survey Bulletin 343.

Bulletin 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp. 3 pls. Reprint of United States Geological Survey Bulletin 366.

Bulletin 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 49 pp. Reprint of United States Geological Survey Bulletin 323.

Bulletin 29. The effect of oxygen in coal, by David White. 80 pp. 3 pls. Reprint of United States Geological Survey Bulletin 382.

Bulletin 30. Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907–8, by C. L. Wright. 41 pp. 9 pls. Reprint of United States Geological Survey Bulletin 385.

Bulletin 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp. Reprint of United States Geological Survey Bulletin 393.

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Bulletin 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 49 pp. Reprint of United States Geological Survey Bulletin 403.

Bulletin 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 32 pp. Reprint of United States Geological Survey Bulletin 412.

Bulletin 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 28 pp. Reprint of United States Geological Survey Bulletin 363.

BULLETIN 37. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests and some foreign specifications for briquetted fuel, by W. F. M. Goss. 57 pp., 4 pls. Reprint of United States Geological Survey Bulletin 363.

TECHNICAL PAPER 1. The sampling of coal in the mine, by J. A. Holmes. 1911. 16 pp.

TECHINICAL PAPER 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp.

TECHNICAL PAPER 3. Specifications for the purchase of fuel oil for the Government with directions for sampling oil and natural gas, by I. C. Allen. 1911. 13 pp.

PUBLICATIONS OBTAINABLE FROM THE SUPERINTENDENT OF DOCUMENTS.

The following technologic publications of the United States Geologic Survey were transferred to the Bureau of Mines for distribution but the supply transferred has been exhausted. Copies may be obtained by sending the price, in cash, to the Superintendent of Documents, Government Printing Office, Washington, D. C.

PROFESSIONAL PAPER 48. Report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1906. In three parts. 1492 pp., 13 pls. $1.50.

BULLETIN 261. Preliminary report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, in St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1905. 172 pp. 10 cents.

BULLETIN 290. Preliminary report on the operations of the fuel-testing plant of the United States Geological Survey at St. Louis, Mo., 1905, by J. A. Holmes. 1906. 240 pp. 20 cents.

BULLETIN 325. A study of four hundred steaming tests made at the fuel-testing plant, St. Louis, Mo., 1904, 1905, and 1906, by L. P. Breckenridge. 1907. 196 pp. 20 cents.

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